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PROGRESS REPORT NO. 3

**RESEARCH INVESTIGATION OF
CORROSION-RESISTANT MATERIALS
FOR ELECTROCHEMICAL CELLS**

DA-44-009-AMC-1452(T)

JANUARY 1968 - JULY 1968

INTERIM REPORT

By

R.R. Sayano, R.A. Mendelson, E.T. Seo and H.P. Silverman

Prepared for

DEPARTMENT OF THE ARMY
U.S. ARMY MOBILITY EQUIPMENT RESEARCH AND DEVELOPMENT CENTER
Fort Belvoir, Virginia 22060

SEPTEMBER 1968



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SYSTEMS GROUP

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SUMMARY

The studies performed during the period 12 January 1968 to 12 July 1968 under Contract DA-44-009-AMC-1452(T) (U.S. Army Mobility Equipment Research and Development Center) are reported.

The diffusion block concept for the rapid preparation of a broad range of alloy systems and for the rapid screening of these alloys for their corrosion resistance in specific environments is verified. Qualitative information on the diffusion-zone characteristics are obtained by visual or optical observations and the chemical composition for areas of high corrosion resistance is determined by electron microprobe analysis.

Two diffusion blocks were constructed and tested. The first block contained cobalt, iron, nickel, chromium, molybdenum, and tungsten; the second block contained niobium, tantalum, vanadium, chromium, molybdenum, and tungsten. The preliminary results indicate good corrosion resistance in phosphoric acid for a binary alloy containing molybdenum and nickel.

TABLE OF CONTENTS

	<u>Page</u>
1. INTRODUCTION	1
1.1 BACKGROUND.	1
1.1.1 Diffusion-Block Concept.	2
1.1.2 Electron Microprobe Analysis	5
1.1.3 Electrical-Resistance and Electrochemical Alloy Evaluation Techniques.	6
2. EXPERIMENTAL TECHNIQUES AND OBSERVATIONS	13
2.1 DIFFUSION BLOCK	13
2.1.1 Fabrication.	13
2.1.2 Heat Treatment (Diffusion)	16
2.1.3 Testing.	16
2.1.3.1 Optical Examination	16
2.1.3.2 Phosphoric Acid Exposure Test	19
2.1.3.3 Post-Exposure Optical Examination	19
2.2 ALLOY FABRICATION AND EVALUATION.	20
2.2.1 Fabrication by Arc-Casting	20
2.2.2 Weight-Loss Measurements	21
2.2.3 Electrical-Resistance Measurements	21
2.2.3.1 Probe Fabrication	21
2.2.3.2 Measurements.	24
3. DISCUSSION	25
3.1 RESULTS	25
3.1.1 Diffusion Blocks	25
3.1.2 Polarized Electrical-Resistance Measurements	26
3.2 CONCLUSIONS	28
3.3 FUTURE WORK	30
REFERENCES	31
APPENDIX A - ELECTRON BEAM MICROPROBE.	32
A1. INSTRUMENT	32
A2. QUANTITATIVE ANALYSIS.	33

1. INTRODUCTION

This interim report describes the studies performed during the period 12 January 1968 - 12 July 1968 under Contract DA-44-009-AMC-1452(T) sponsored by the U. S. Army Mobility Equipment Research and Development Center.

The major emphasis of the work performed under this contract has been on the fabrication and evaluation of alloys for use in electrochemical energy conversion devices operating with hot, concentrated phosphoric acid or a fused salt. Results obtained during the program include:

- Development of the differential corrosion probe for electrical-resistance (Corrosometer) measurements.
- Demonstration of the feasibility of the diffusion-block technique for fabricating test alloys.
- Application of the electrical-resistance method to polarized test specimens.

As a result of work sponsored under the present contract two binary alloys systems, iron-molybdenum and nickel-molybdenum, have been identified as being particularly corrosion resistant. The high corrosion-resistance of these alloy systems is particularly interesting because of the low cost of the materials involved.

1.1 BACKGROUND

The study of the compatibility of materials with electrolytes used in energy conversion devices is an important aspect in the development of low-cost, high-energy batteries, fuel cells, and other energy-storage

devices. The problems associated with the lifetimes and costs of these devices are mainly a result of the highly corrosive nature of the electrolyte at the elevated temperatures that must be maintained in order to obtain the desired device performance. Corrosion limits the cell performance, not only by the degradation of the mechanical properties of the materials, but more importantly by the degradation of the electrochemical activity of the electrode catalyst, which results in reduced output and lifetime of the cell. The proper selection of the materials of construction for the energy storage device will lead to increased cell life, reduced costs, and higher performance. In addition, a method by which the corrosion rate can be rapidly determined for materials exposed to this severe environment is highly desirable for determining material compatibility economically and efficiently.

Corrosion resistant alloys are identified by:

- 1) Exposing diffusion-block cross-sectional samples to a corrosive environment followed by microprobe, optical and/or chemical analysis of the more promising corrosion-resistant areas, and
- 2) Measuring corrosion rates of arc-cast samples of the promising alloys by electrical-resistance techniques based on the use of potentiostated differential probes.

1.1.1 Diffusion-Block Concept

The selection and optimization of an alloy composition compatible with a specific environment usually requires the evaluation of a large number of alloys - an expensive and tedious process. The "diffusion-

"block" concept provides an efficient approach to preliminary alloy evaluation.

A diffusion block, as used within the context of this report, comprises individual metallic specimens (elements) stacked in a two-dimensional matrix array. Figures 1 and 2 are photographs of typical blocks. When heated at high temperature in an inert atmosphere or vacuum, this diffusion-block array forms multicomponent alloys between individual elements at their original interfaces.

The interdiffusion of these materials obeys Fick's diffusion laws which relate time, temperature, and diffusion distance. High temperatures are used to obtain the broad range of desired alloy compositions in minimum time. Exposure to high temperature results in a series of equilibrium alloys that exist between every metallic pair and represent all the single-phase regions within a given binary alloy system. All intermetallic phases of the solid solution regions of the binary system (or higher order systems) are, therefore, present in varying quantities throughout the region of the original interface. The extent of diffusion in a given block is determined by the temperature and the mutual solubility of the respective elements. The diffusion process is continued for a sufficient length of time so that a wide diffusion zone results permitting maximum resolution of alloy compositions.

Following the hot diffusion treatment, a section of the block is removed and exposed to a corrosive media of interest to determine the relative corrosion-resistant contours of the alloy systems. The

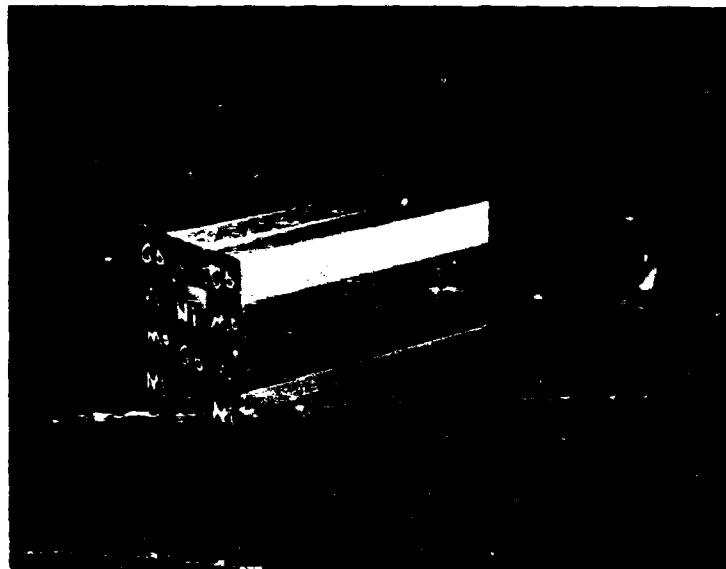


Figure 1. Stacking Configuration of the Elements Niobium, Chromium, Tungsten, Nickel and Molybdenum.

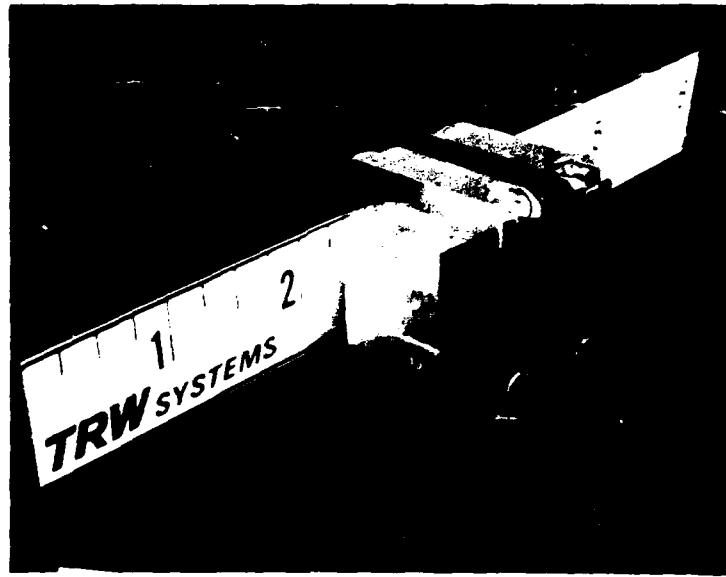


Figure 2. Diffusion Block in Molybdenum High-Temperature Clamp.

chemical (alloy) composition of the most resistant regions is obtained by chemical or electron microprobe analysis.

1.1.2 Electron Microprobe Analysis

The high resolution and selectivity of electron microprobe analysis provides an excellent means to determine the composition of diffusion zones.

In electron microprobe analysis, within the spectrometer a finely focussed, primary electron beam ($\sim 0.5 \mu\text{m}$ diameter) is directed at the specimen causing electron excitation within the target material over a volume of $1-10 \mu\text{m}^3$. When these excited electrons return to their ground states, characteristic electromagnetic radiation in the form of x-rays is emitted. The x-ray spectrum is analyzed by wavelength dispersion (crystal) techniques and energy dispersion (pulse-height analysis) techniques. Each element has its characteristic x-ray spectrum which is independent of the state of aggregation of the element.

The intensity of the x-ray, at a given wavelength is related to the concentration of the element producing the x-radiation in the sample. By determining the x-ray intensity of a standard sample (usually a pure element) and background, the weight (mass) fraction of the given element at the interrogated point can be computed. The relative accuracy of 2% in the concentration can be obtained by absorption-fluorescence corrections. Analysis can be performed for all elements above atomic number of five with sensitivities (lower limits of detection) ranging from one part in 10^5 (0.001%) to one part in 10^3 (0.1%) depending on substance analyzed, matrix and spot size.

As an example, the electron microprobe analysis of a cobalt-chromium diffusion zone formed at 1150 °C (Figure 3) is summarized in Figure 4. Alloys A and B represent the cobalt-rich and chromium-rich terminuses, respectively, of the σ -phase, a non-stoichiometric intermetallic compound. Alloys C and D are the chromium-rich and cobalt-rich terminal solid solutions, respectively.

1.1.3 Electrical-Resistance and Electrochemical Alloy Evaluation Techniques

Once the candidate alloys are selected, a means to rapidly determine their compatibility in a given environment is required. The electrical-resistance method can be used to rapidly determine corrosion rates greater than one mil per year. For corrosion rates of less than one mil per year, electrochemical techniques can be used. Between these two methods, the electrical-resistance is the easier to carry out and requires minimum instrumentation. The electrochemical methods, even though requiring more instrumentation, provide additional insight into the corrosion mechanism of the test specimens through examination of the potential-current or polarization curves.

The basic circuitry of the electrical-resistance method consists of two electrically-conducting elements (the corrosion-measuring probe) that constitute two arms of a modified wheatstone bridge. The probe, constructed of the material of interest, is formed into a strip, wire, or tube to which electrical leads are attached at each end and at the center. Under normal conditions, one-half of the probe, labelled the reference arm, and all electrical leads are protected from the corrosive



Figure 3. Microstructure of Diffusion Zone ($\times 50$).
Probe scan was 30° to the interface.

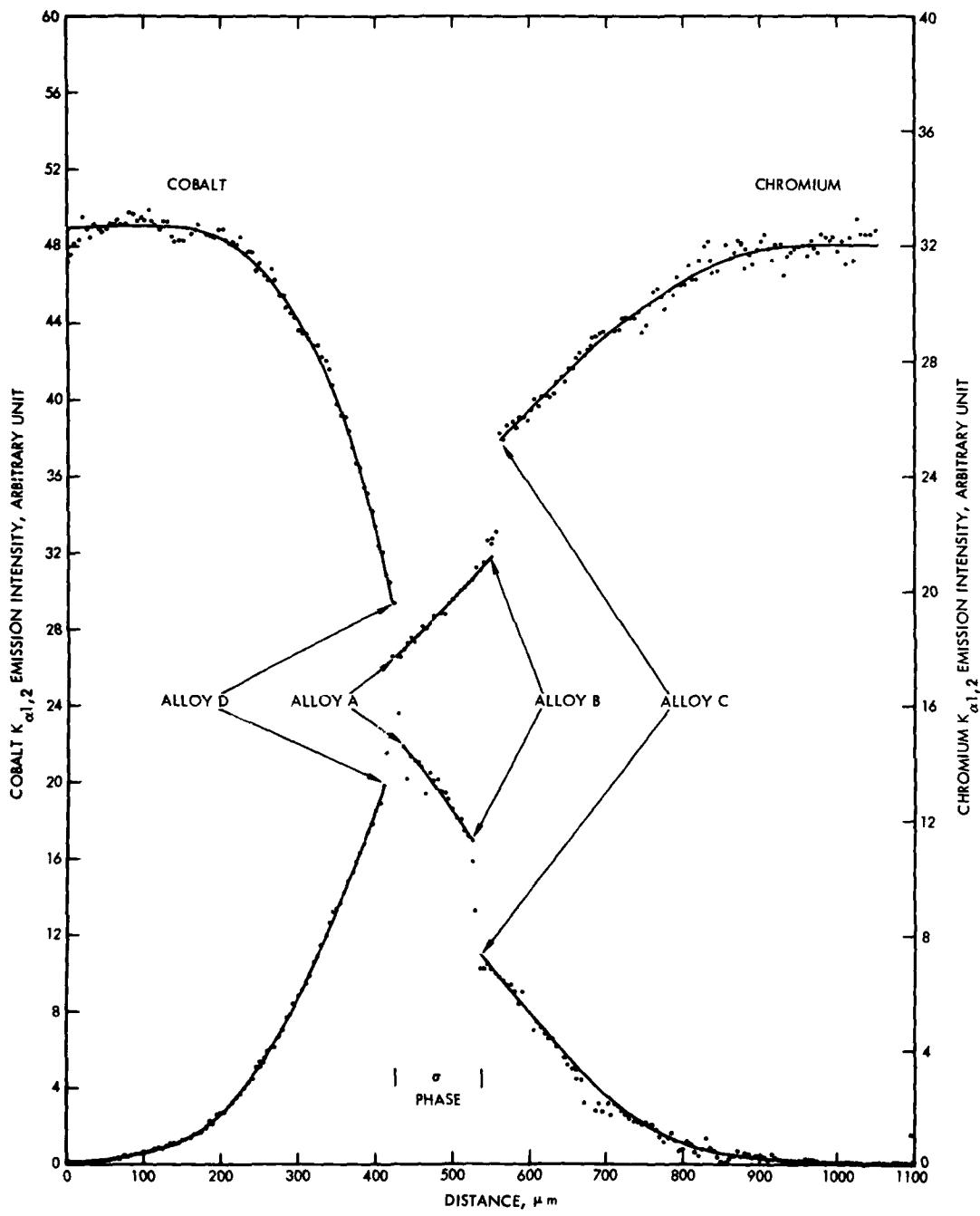


Figure 4. Concentration-Penetration Curve for Cobalt-Chromium Diffusion Couple at 1150 °C.

environment by an impervious, chemically inert coating. Measurements are made by applying an alternating current across the length of the probe through one set of leads and measuring the resistance through the other set of leads. As the exposed part of the probe, labelled the measuring arm, corrodes, its cross-sectional area decreases resulting in an increase in electrical resistance. The change in resistance measured by the bridge type instrument can then be related to the amount of metal lost through corrosion.

The electrical-resistance method requires compensation for changes in the resistance due to temperature fluctuations. This compensation is accomplished simply by using a reference arm on the probe protected from the environment by a coating. This approach requires a coating that is impervious, resistant to chemical attack, and resistant to thermal shock, for each environment studied. However, for environments which are too aggressive for any type of coating (e.g., fused salts, hot phosphoric acid), a new type of probe (differential) was developed that requires no protective coating and incorporates all the advantages of the conventional coated probes (1).

The differential probe contains two sensing elements with different initial thicknesses. The basic design is shown in Figure 5, where the thicknesses have been exaggerated. The entire probe can be made of one piece of metal to avoid problems encountered with contact corrosion. With no protective coating, corrosion takes place uniformly over the entire surface of the probe immersed in the corrosive environment. As corrosion occurs, the cross sections become thinner by equal amounts; but, because of the different geometries, the resistances of the two

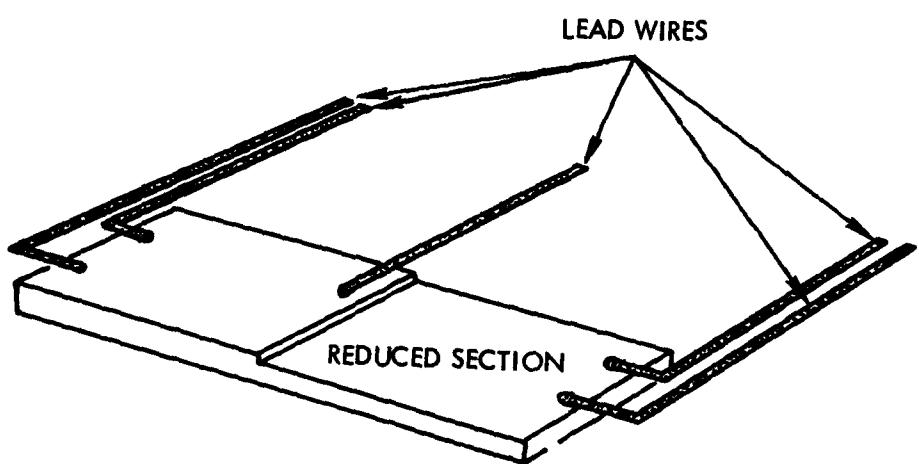


Figure 5. Differential Resistance Probe
for Corrosion Studies.

sensing elements increase at different rates. The change in the resistance ratio of the two elements is monitored as a function of time. The corrosion rate is calculated from the data. A mathematical analysis of the method was presented in the previous report (1).

The application of electrochemical theory to the corrosion process, assumes the existence of regions on the test specimen (electrode) surface in which oxidation (dissolution of metal) and reduction processes occur. These regions are further assumed to be uniformly distributed over the entire surface of the corroding metal.

The net rate of oxidation or reduction can be controlled externally by the application of potential to the specimen (with respect to a reference electrode). The amount and direction of the current supplied to maintain a given potential represents the net rate of either the oxidation or reduction process.

Besides making it possible to determine extremely low corrosion rates, electrochemical techniques can be useful in obtaining information on the corrosion mechanism. The shape of the potential-current or polarization curve (for overvoltage $E < |2 V|$), is useful in determining not only the environmental effects (e.g., temperature and acidity) but also the metallurgical effects on corrosion rates. For example, the effects of temperature, pH, and alloy composition on the passivity of metal can be investigated by means of the polarization curves. On the practical side, a polarization curve, determined for a specific material exposed in a given environment, is useful in predicting the actual

behavior of the material such as the rate of metal dissolution under polarized (applied external potential) conditions.

2. EXPERIMENTAL TECHNIQUES AND OBSERVATIONS

2.1 DIFFUSION BLOCK

2.1.1 Fabrication

Two blocks of six elements each were prepared using a two dimensional four-by-four array. Calculations for the case of six different elements indicate that 15 unique binary and 15 unique quaternary combinations are possible:

$$m = \frac{n(n - 1)(n - 2) \dots (n - p + 1)}{p!} = \frac{n!}{p!(n - p)!}$$

where m is the number of combinations, n is the number of elements, and p is the grouping (i.e., binary, ternary). For the binary cases (n = 6; p = 2),

$$m = \frac{6!}{2!(6 - 2)!} = 15$$

For the quaternary case (n = 6; p = 4),

$$m = \frac{6!}{4!(6 - 4)!} = 15$$

Block A contains tungsten, molybdenum, chromium, iron, cobalt, and nickel; Block B contains tungsten, molybdenum, chromium, tantalum, vanadium, and niobium. A photograph of both blocks is shown in Figures 6b and 6c, respectively. Tungsten, molybdenum, and chromium are common to both blocks.

Block A contains all possible binary alloy combinations and the following seven quaternary alloy combinations:

Cobalt, chromium, iron, nickel

Cobalt, chromium, iron, tungsten

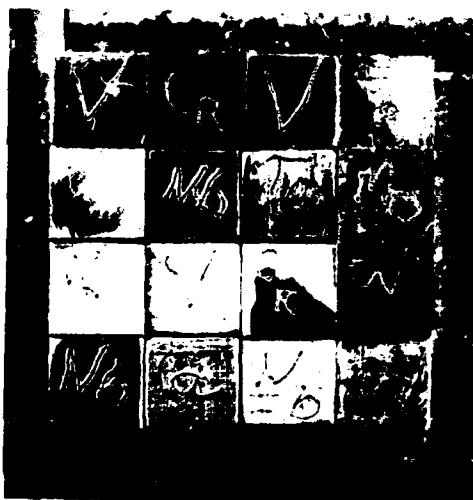
Cobalt, chromium, nickel, tungsten



a



b



c

Figure 6. Multi-component Diffusion Blocks. In (a), diffusion blocks are shown held in high-temperature molybdenum clamps. Details of the stacking arrays for Block A (Ni, Cr, W, Co, Fe, and Mo) and Block B (V, Cr, W, Nb, Ta, and Mo) are shown in (a) and (b), respectively.

Cobalt, iron, molybdenum, nickel

Cobalt, molybdenum, nickel, tungsten

Chromium, iron, molybdenum, nickel

Chromium, iron, molybdenum, tungsten

Similarly, there are all the binary alloy combinations and seven
quaternary alloy combinations for Block B:

Chromium, molybdenum, niobium, vanadium

Chromium, molybdenum, tantalum, tungsten

Chromium, niobium, tantalum, vanadium

Chromium, niobium, tungsten, vanadium

Chromium, niobium, tantalum, tungsten

Molybdenum, niobium, tantalum, vanadium

Molybdenum, niobium, vanadium, tungsten

Materials were obtained from commercial sources and were 99.8%
pure or better:

Chromium, Leico Industries Inc., 99.9%

Cobalt, Kulite Tungsten Co., 99.9%

Iron, Crucible Steel Co., 99.9%

Molybdenum, Fansteel Metallurgical Corp., 99.95%

Nickel, International Nickel Co., 99.8%

Niobium, Kawecki Chemical Co., 99.8%

Tantalum, Fansteel Metallurgical Corp., 99.9%

Tungsten, Fansteel Metallurgical Corp., 99.95%

Vanadium, Stellite Div., Union Carbide Corp., 99.95%

The metallic elements of the blocks were machined by standard milling and electric-discharge (Elox) techniques into units 0.1875 in. \times 0.1875 in. \times 2.5 in. The clamp for the blocks, fabricated from molybdenum, was designed to provide compression at ambient and elevated temperatures.

2.1.2 Heat Treatment (Diffusion)

Diffusion across the interfaces was effected by heating the blocks in vacuum; Block A was heated at 1200 °C in a conventional tube furnace and Block B was heated at 1600 °C in a Brew High-Temperature Vacuum Furnace. Temperature and pressure were maintained within ± 2 °C and below 10^{-4} torr, respectively. Temperatures were chosen to avoid melting any components or alloys.

2.1.3 Testing

2.1.3.1 Optical Examination

At regular intervals in the heat treatment process, the blocks were cooled and cross-sectional samples were cut from the blocks and examined optically under a microscope. These examinations provided a check on the progress of the interdiffusion processes. Figures 7 and 8 show typical interdiffusion at the interfaces from each of the blocks after 100 and 300 hours of heat treatment. From the photomicrographs, the growth of the diffusion zones as a function of time is apparent. Since the formation of alloys is dependent on mass transfer of the starting materials, larger diffusion zones give greater ranges of identifiable alloys.

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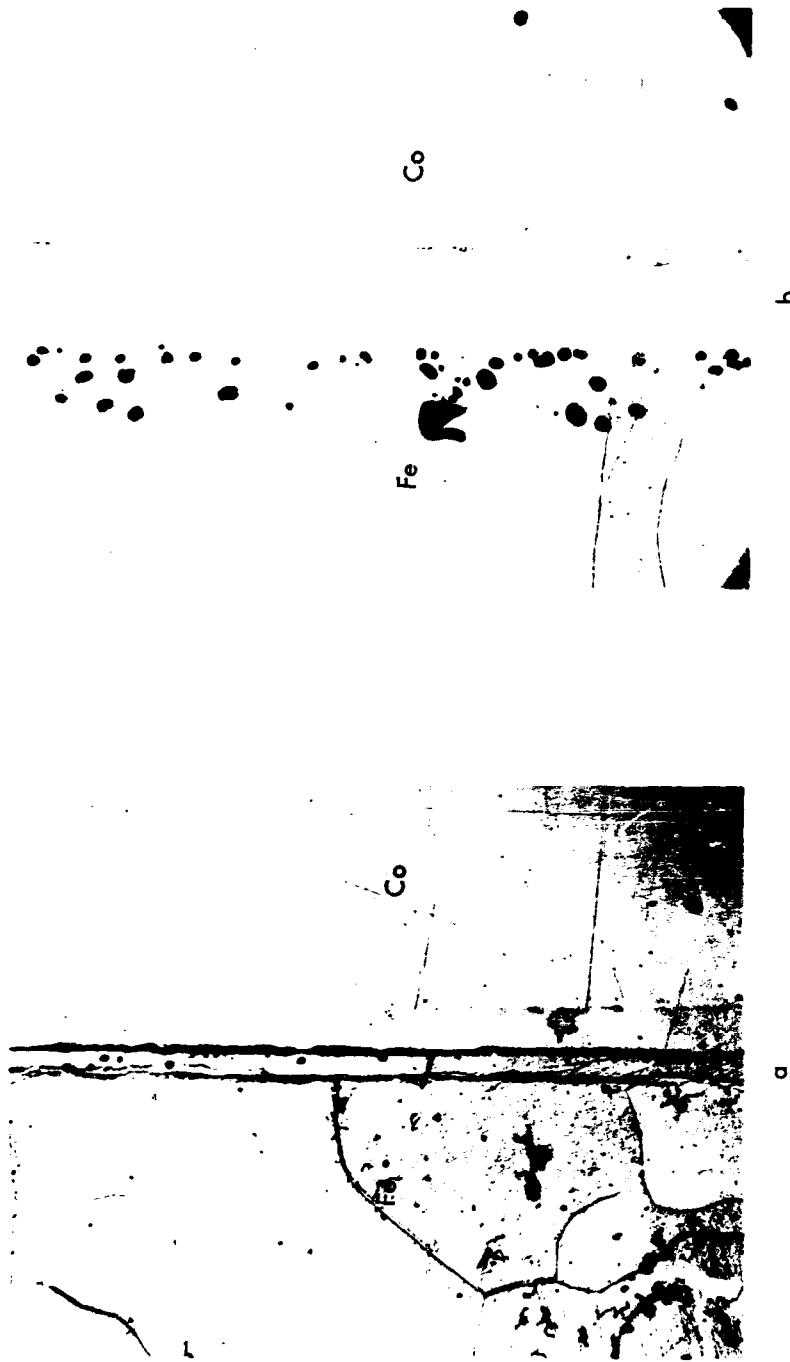


Figure 7. Photomicrographs of Fe-Co Binary Diffusion Zone ($\times 100$). Photographs were taken after
(a) 100 hours and (b) 300 hours of heat treatment at 1200°C .

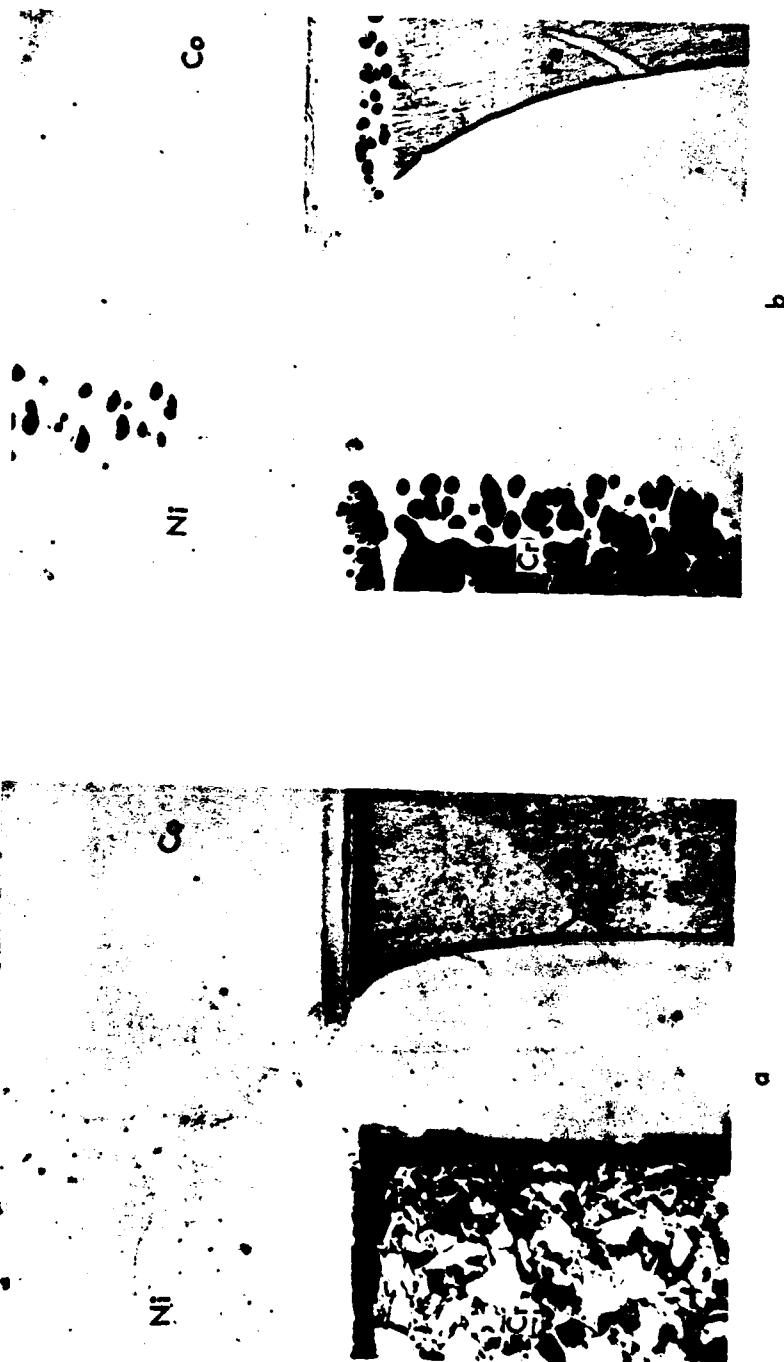


Figure 8. Photomicrographs of Ni-Co-Cr-Fe Quaternary Diffusion Zone ($\times 100$). Photographs were taken after (a) 100 hours and (b) 300 hours of heat treatment at 1200°C .

2.1.3.2 Phosphoric Acid Exposure Test

After optical examination, the sections of the diffusion blocks were immersed in deaerated phosphoric acid at 200 °C. The phosphoric acid medium was prepared by boiling the "as received" 85% phosphoric acid (Mallinckrodt, reagent grade) under an argon atmosphere until its boiling temperature reached 225 °C. The acid was then thermostated at 200 ± 2 °C. The cell used for preparation of the acid and testing of the blocks was similar to the one used in the previous program (1). A block cross-section was placed on a perforated Teflon platform and immersed in the hot acid.

2.1.3.3 Post-Exposure Optical Examination

After exposure to the phosphoric acid at 200 °C, the specimens from each of the blocks were examined both visually and by electron microprobe analysis to determine the most corrosion-resistant areas. The "hill and valley" effect that would result from the relative corrosion resistance of the diffusion-formed alloys and the parent metals was easily observed. Indeed, in Block A, pure iron and pure chromium were completely etched away and only the resistant alloys of these elements remained. Visual examination of the cross-section removed from Block A indicated that the most resistant alloys were of iron-molybdenum and molybdenum-nickel composition. Other combinations are currently being examined in greater detail to determine their relative corrosion resistance. The Block B cross-sectional sample was exposed to the acid for a much longer period of time and it revealed two areas which were more corrosion resistant than remaining areas of the block. However, the

two compositions as determined by the microprobe analysis were extremely high in tantalum content. The results of the exposure and post exposure examination show that some heretofore unexpected, inexpensive alloy combinations are resistant to phosphoric acid at 200 °C.

Electron microprobe analyses were performed using the instrument described in Appendix A. The microprobe was operated in both the spectral scanning and spatial step-scan analysis modes. Absorption and fluorescence corrections were made.

2.2 ALLOY FABRICATION AND EVALUATION

2.2.1 Fabrication by Arc-Casting

Based upon microprobe analysis and on examination of binary phase diagrams, a series of promising iron-molybdenum and nickel-molybdenum binary alloys were prepared. Samples (10 to 15 g) of appropriate composition were melted in an electron-beam furnace. The possibility of contamination from both the electrode and the atmosphere are reduced because the electrode is not consumed and the melting is effected in vacuum (10^{-4} torr). Uniform cast structure was achieved by inverting and remelting the buttons of alloy several times.

The buttons are then sectioned and examined for homogeneity. If segregation was observed in the alloy, the alloy was discarded and another button of the same composition prepared.

2.2.2 Weight-Loss Measurements

The candidate alloys in the form of buttons were carefully weighed before and after exposure to concentrated phosphoric acid at 200 °C.

The results are given in Table 1. The reported corrosion rates are only approximate because the surface area of the button could not be accurately measured.

2.2.3 Electrical-Resistance Measurements

2.2.3.1 Probe Fabrication

All of the Corrosometer probes prepared for measuring corrosion rates are of the differential design developed earlier in this program (1). The differential probe was made by chemically removing approximately half the thickness from one half of the probe. The probe design used is shown in Figure 5.

The actual fabrication of the probes fell into two categories. The first was for those alloys which were ductile enough to be cold-rolled into strips. Fabrication of probes from these alloys involved cutting a piece approximately 1 in. × 1/4 in. from the strip and etching it to the desired configuration. For the non-ductile alloys, a section was cut from the alloy button and ground to the final shape. In both cases, platinum lead wires were attached by spot welding. A list of probes is given in Table 2.

Table 1. Weight Loss for Alloy Buttons and Approximate Corrosion Rates

<u>Composition w/o</u>	<u>Weight Loss (g)</u>	<u>Exposure Time (hr)</u>	<u>Corrosion Rate (mpy)</u>
100 Ni	0.6493	3.0	27,966
37 Mo-Ni	-0.0039 ⁽¹⁾	4.5	--
30 Mo-Ni	0.0002	4.5	3.30
25 Mo-Ni ⁽²⁾	-- ⁽³⁾	4.5	--
20 Mo-Ni ⁽⁴⁾	0.0293	4.5	490
20 Mo-Ni ⁽⁵⁾	0.0777	4.4	1,415
20 Mo-Ni ⁽⁴⁾	0.0273	4.4	495
30 Mo-Fe	0.1798	2.5	4,809

- Notes: (1) Increased in weight
 (2) Inhomogeneous sample - contained void and secondary phase
 (3) Undetectable for duration of test
 (4) As rolled
 (5) Annealed

Table 2. Electrical-Resistance Probes

<u>Composition (w/o)</u>	<u>Lead Wire</u>	<u>Fabrication</u>	<u>Thickness (mm)</u>	
			<u>Reference</u>	<u>Measuring</u>
20 Mo-Ni	Pt	Rolled	0.305	0.175
20 Mo-Ni	Pt	Rolled-Annealed	0.360	0.211
20 Mo-Ni	Ta	Rolled-Annealed	0.314	0.177
30 Mo-Ni	Pt	Rolled	0.435	0.194
37.5 Mo-Ni	Pt	Milled	1.000	0.500
35 Mo-Ni	(to be fabricated)			
37 Mo-Ni	(to be fabricated)			
0-52 Mo-Fe	(to be fabricated)			

2.2.3.2 Measurements

Preliminary electrical-resistance (Corrosometer) measurements have been made using conventional measurements techniques, i.e., without applied potential, as described earlier (1). Future measurements will be made with an externally applied potential. Newly developed techniques with applied potential are described in Section 3.1.2.

3. DISCUSSION

3.1 RESULTS

3.1.1 Diffusion Blocks

Block A contained Co, Fe, Ni, Cr, Mo and W. The block was heat-treated in a vacuum environment for 300 hours at 1200 °C resulting in the formation of binary, ternary and quaternary alloys by diffusion at the original interfaces. A section of this block was exposed to 200 °C phosphoric acid to determine which, if any, of the alloy combinations would show good corrosion resistance. Visual examination of the block after exposure to the acid revealed several "good" areas. These areas represent, in decreasing order of resistance (excluding Mo and W), alloys of Mo-Ni, Fe-Mo and Co-Cr and the pure metals Co, Cr, Fe and Ni. The verification of these alloys and the determination of their composition were made with the electron microprobe.

At this time, detailed studies have been performed on the molybdenum-nickel alloy system. The microprobe analysis of this system showed that the most resistant area was the intermetallic compound MoNi. Previous experience in working with intermetallic compounds has shown that they are difficult to produce and even more difficult to fabricate. To avoid the fabrication difficulties encountered with intermetallic compounds and yet examine the Mo-Ni system, a series of conventional Mo-Ni alloys were prepared. The alloy compositions ranged from 20 to 62 w/o molybdenum. Preliminary corrosion data obtained with the Corrosometer shows a corrosion rate of less than 1 mil per year for the alloy containing 37 w/o Mo. The 37 w/o Mo-Ni alloy in the weight-loss test

did not give a meaningful corrosion rate value; its weight increased during its short exposure time. Additional work is still in progress on this and other alloy systems from Block A.

Block B contained Nb, Ta, V, Cr, Mo and W. The diffusion within this block was effected by heating at 1600 °C in vacuum for 300 hours. Once again, interdiffusion across the original interfaces formed an infinite series of alloys. A section of this block was also exposed to the acid media to determine the most resistant areas. Because of the inherently high corrosion resistance of most of the elements used in this block the post-test examination was more difficult than for Block A. However, two compositions were found to be more resistant to phosphoric acid and were identified by electron microprobe analysis. The composition of these alloys were 78 w/o Ta, 1.8 w/o Cr, 6 w/o Nb, 13.7 w/o V; and 60.5 w/o Ta, 4.6 w/o Cr, 34.9 w/o V. Alloys with these compositions are being fabricated at this time. Visual examination of Block B revealed that:

- 1) Pure molybdenum appears to corrode at a lower rate than pure tantalum, and
- 2) Alloys with high concentrations of niobium show evidence of hydrogen embrittlement and thus would not be applicable for long term exposure to phosphoric acid media.

3.1.2 Polarized Electrical-Resistance Measurements

The alloy or alloys which exhibit corrosion rates of less than 1 mpy will be subjected to polarized Corrosometer measurements.

The proposed schematic diagram for the experimental procedure is shown in Figure 9. A potentiostat is used to maintain a constant voltage

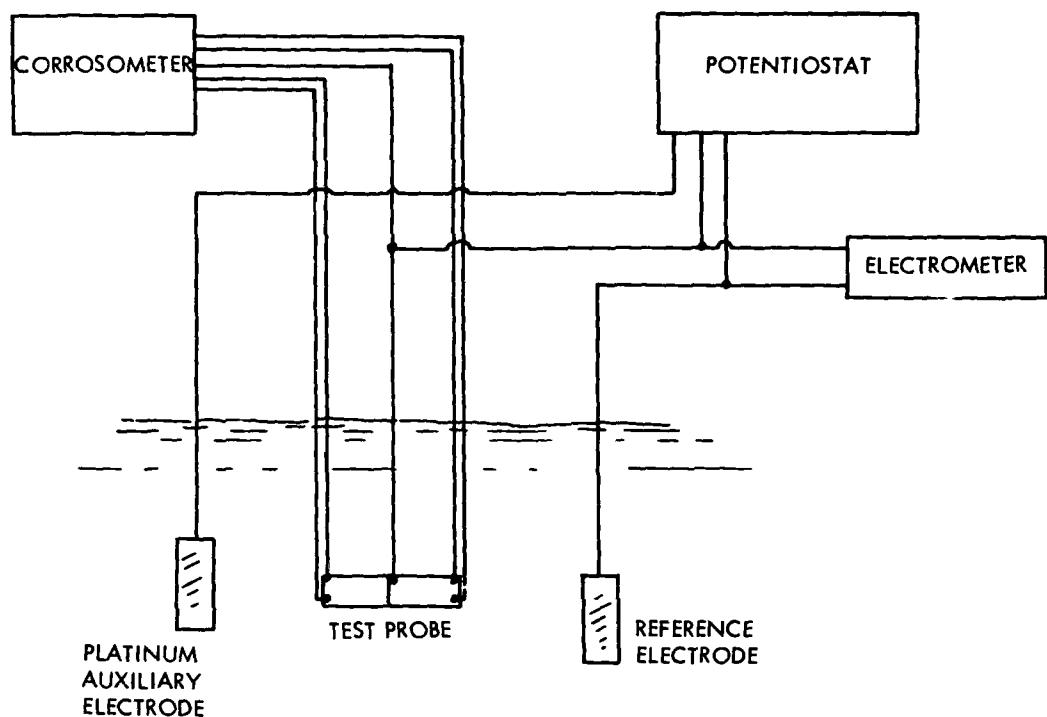


Figure 9. Schematic Diagram for Polarized Electrical-Resistance Measurement.

of 0.1 and 0.4 V between the test specimen (in the form of a Corrosometer probe) and a reference electrode. A high input impedance electrometer is used to measure the electrode potential without drawing any current between the test and reference electrodes.

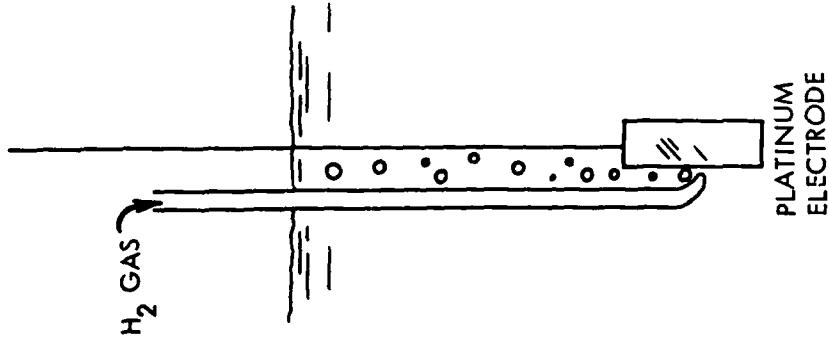
Since no suitable reference electrode is available for use in concentrated phosphoric acid at 200 °C, the success of this part of the program will depend on the choice of the reference electrode. The suitability and stability of a reversible hydrogen electrode (rhe) diagrammed in Figure 10a (a platinized platinum placed in the same environment as the test specimen but saturated with hydrogen) will be checked. An alternate reference electrode, the so-called "polarized reference electrode (2)," is diagrammed in Figure 10b. The use of this electrode requires the passage of constant current (e.g., 1 mA/cm^2) between two platinum electrodes such that hydrogen gas is evolved at the electrode which is taken as the "reference". The stability of these reference electrodes will depend on the stability of the environment and reversibility of the electrochemical reactions at the platinum surface.

3.2 CONCLUSIONS

Based upon the experimental work performed so far under this contract we can tentatively conclude that:

- 1) The diffusion-block concept is a valid and rapid method for preparing a broad range of alloy systems for screening for corrosion resistance in a specific corrosive environment.
- 2) An alloy of molybdenum and nickel has good corrosion resistance in phosphoric acid.

a



b

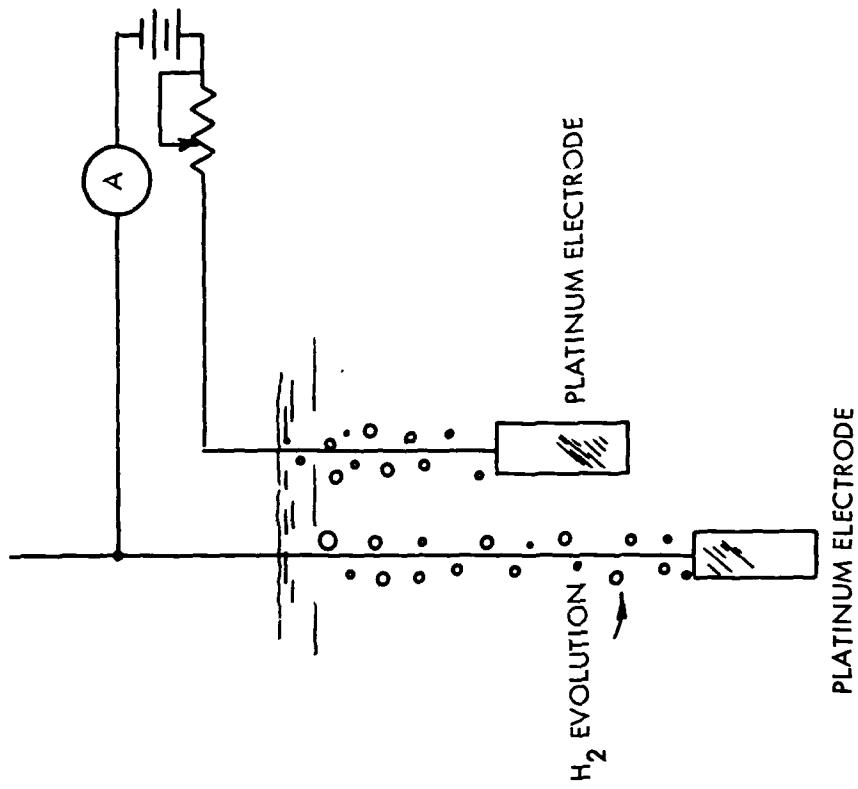


Figure 10. Two Types of Reference Electrodes for Polarized Electrical-Resistance Measurement. The reversible hydrogen electrode (rhe) and polarized reference electrodes are diagrammed in (a) and (b), respectively.

- 3) Visual or optical observations provide qualitative inspection of the diffusion zone characteristics.
- 4) Electron microprobe analysis permits the determination of alloy composition for areas of high corrosion resistance.

3.3 FUTURE WORK

The remainder of this program is concerned with:

- 1) Further evaluation of Fe-Mo and Ni-Mo binary alloy systems and at least one of the promising higher component alloys. Weight-loss tests will be conducted for Fe-Mo alloys with up to 52 w/o Mo. An attempt will be made to fabricate one of the higher-order alloys: Co-Fe-Cr-Ni (Block A), Ta-Cr-Nb-V (Block B), or Ta-Cr-V (Block C). The exact compositions of promising higher order alloys will be obtained from electron microprobe analysis.
- 2) Determination of electrical-resistance (Corrosometer) data for Fe-Mo and Ni-Mo binary alloys and at least one of the higher order alloys (if fabricable).
- 3) Further development of the "polarized (potentiostated)" electrical-resistance technique which requires a stable, high-temperature reference electrode and application of the technique to any alloys exhibiting less than 1 mpy corrosion rate.
- 4) Compilation of corrosion data for Fe-Mo and Ni-Mo alloys as a function of alloy composition.

REFERENCES

1. TRW Systems Group, "Research Investigation of Corrosion-Resistant Materials for Electrochemical Cells," Final Report, January 1966 - January 1967, Contract DA-44-009-AMC-1452(T), U. S. Army Engineering Research and Development Laboratories, Fort Belvoir, Virginia 22060.
2. J. Giner, "A Practical Reference Electrode," *J. Electrochem. Soc.* 111, No. 3, 376-7 (March 1964).

APPENDIX A
ELECTRON BEAM MICROPROBE

A1. INSTRUMENT

The TRW Systems Group Electron Beam Microprobe facility consists of an Applied Research Laboratory (Glendale, California) Model EMX Electron Microprobe. The highly collimated primary electron beam is less than 0.5 μm with beam energies of 2 to 30 keV. The beam diameter at the sample surface is less than 1 μm . The emitted x-rays are analyzed by a two wavelength x-ray spectrometer with capability of detecting all elements except hydrogen, helium, lithium, and beryllium. Each x-ray spectrometer is equipped with pulse height analysis systems. The microprobe also has back-scattered electron detector, sample current monitor, and micrometer sample stage with spatial resolution of $\pm 5 \mu\text{m}$. The sample chamber can hold up to eight metallurgical specimens at once for analysis. The electron microprobe can be operated in three modes: Spectral Scanning Mode - the electron beam and the sample are held stationary while wavelength ranges ($1\text{-}27 \text{\AA}$) are scanned with the two wavelength spectrometers; Spatial Step Scan Analysis - spectrometers are kept at a constant setting (either at peak or at background) and the sample is moved in steps along a straight line under the stationary electron beam; and Beam Scanning Mode - beam is scanned in horizontal and vertical axis to give a "chemical map" of the surface. Magnification of the images is from $250\times$ to $8,000\times$.

The specimens to be analyzed are mounted in conductive copper molding materials with special care taken to maintain flatness and perpendicularity. The specimens are polished by conventional

metallurgical techniques with no etchant being used. The unetched samples are placed in the sample chamber.

A2. QUANTITATIVE ANALYSIS

The computation of mass fraction of an element in a multicomponent specimen starts with the intensity ratio of a given spectral line.[†] That is, if \underline{J}_i represents x-ray intensity generated within a specimen, the important parameter is the ratio

$$\underline{J}_i / \underline{J}^{\circ}_i = c_i \quad (1)$$

where c_i is the mass fraction of element i and \underline{J}_i and \underline{J}°_i are the intensities of the spectral line of a given wavelength from the sample and standard specimen of element i , respectively.

^{*} Castaing showed that this ratio is indeed the mass fraction of the element i in the sample if the intensity values are the intensities generated in the samples due to primary electron excitation only (no fluorescence effects). The measured intensities are of course diminished due to sample absorption which, for the given wavelength, is a function of the composition of the material through which the x-rays must traverse while traveling toward a detector. TRW uses the absorption relation of Philibert^{**} given by the expression

$$f(x) = \{(1 + x/\sigma)[1 + h(1 + x/\sigma)]\}^{-1} \quad (2)$$

[†] It will be assumed that drift and dead-time corrections have been made.

^{*} R. Castaing, "Application des Sondes Electroniques a une Methode D'Analyse Ponctuelle Chimique et Crystallographique." ONERA Publication 55, 1952.

^{**} J. Philibert, "A Method for Calculating the Absorption Correction in Electron-Probe Microanalysis," in "X-ray Optics and X-ray Microanalysis," H. H. Pattee, V. E. Cosslett, and A. Engstrom, eds., Academic Press, New York, New York, 1963, pp. 379-392.

In the relation, the quantities have the following meanings:

1. $h = 1.2 \bar{A}/\bar{Z}^2$ where \bar{A} and \bar{Z} are, respectively, the average atomic weight and average atomic number of the sample.

The average is computed on an atomic basis.

2. σ is a modified Lenard coefficient and is a function of only the primary electron energy (operating voltage) V and the critical excitation energy V_0 for the spectral line in question. σ is calculated from the relation

$$\sigma = 2.39 \times 10^5 / (V^{1.5} - V_0^{1/5})$$

where the voltages V and V_0 are expressed in kilovolts.

3. x is the absorption parameter given by

$$x = (\mu/p)_i \csc \theta$$

for a pure element, or by

$$x = \csc \theta \sum_i (\mu/p)_i C_i$$

for a multi-component sample. In the expressions, μ/p is the mass absorption coefficient for element i at the wavelength in question, θ is the x-ray detector take-off angle (52.5° for TRW), and C_i is the mass fraction of element i .

In order to compute h and x , it is necessary to know the sample composition, the very quantity that is the unknown. The procedure is to compute a first order mass fraction for each element from the measured intensity ratios and then to use this composition as a basis for computing h and x .

The function $f(x)$ relates the measured intensity and the generator intensity as follows:

$$I_i = J_i f_i(x)$$

Thus,

$$I_i/I^{\circ}_i = (J_i/J^{\circ}_i)[f_i(x)/f^{\circ}_i(x)]$$

or, from Equation 1,

$$\begin{aligned} C_i &= (I_i/I^{\circ}_i)[f^{\circ}_i(x)/f_i(x)] \\ &= (\text{measured ratio})(\text{absorption ratio}) \end{aligned} \quad (3)$$

Equation 3 is the basic relation that is used for making absorption corrections.

In multi-component samples the situation frequently arises that one element, j has a characteristic radiation that will excite the characteristic radiation of element i (fluorescence). In this case, the technique of Birks *** is most conveniently used in desk-type calculations to make corrections. The procedure is to amend Equation 3 as follows:

$$C_i = (I_i/I^{\circ}_i)[f^{\circ}_i(x)/f_i(x)](1 + k)^{-1} \quad (4)$$

where k , the fluorescence correction is given by

$$k = 0.6 C_j E_{ij} (\mu_{ij}/\mu'_j) [(v - v_{oj})/(v - v_{oi})]^2 \quad (5)$$

In the previous expression,

C_j is the weight fraction of element j (the one responsible for fluorescence in element i)

*** L. S. Birks, "Electron Probe Microanalysis," Interscience Publishers, New York, New York, 1963, pp. 118-119 and 186 ff.

E_{ij} is the number of i -quanta emitted per incident j -quanta
(tabulated by Birks),

μ_{ij} is the mass absorption coefficient of element i for the
characteristic x-rays from element j ,

μ'_i is the total mass absorption coefficient of the specimen for
the characteristic x-rays from element j , and

v_{oj} and v_{oi} are the critical excitation voltages for elements j
and i , respectively.

Thus, the correction procedure consists of the reiterative use of
Equations 1 to 5 until convergence in composition is obtained. In
practice, one cycle in the iterative procedure is usually sufficient
to arrive at a composition that is good to within $\pm 5\%$ of the correct
value.

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